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(54) Process for improving the static and dynamic mechanical properties of (alpha + beta) titanium alloys.

(57) The process relates to the improvement of the static and dynamic mechanical properties of $(\alpha + \beta)$ titanium alloys by thermomechanical treatment, wherein the alloys produced by melting and forging and/or hot isostatic pressing of powders are deformed by more than 60 % with simultaneous strain-hardening at a temperature just above the recrystallization temperature of the relevant alloys in one or more steps, with structure stress-relief heatings being performed without complete recrystallization between these individual steps, the shaped part is then tempered for 2 to 4 min near the transus of the alloy, quenched and then aged at temperatures in the range of from 400 to 600°C.

PROCESS FOR IMPROVING THE STATIC AND DYNAMIC MECHANICAL PROPERTIES OF $(\alpha+\beta)$-TITANIUM ALLOYS

The invention relates to a process for improving the static and dynamic mechanical properties of $(\alpha+\beta)$-titanium alloys by thermomechanical treatment.

It is known that the mechanical properties of titanium can already be improved by means of alloying additions. By the addition of certain alloying elements the transformation temperature of titanium from the α into the β phase can be raised or lowered, i.e., a distinction is made between alloying additions that stabilize either the α or the β phase. For example, aluminum is among the α-stabilizing alloying elements and is dissolved as a substitutional mixed crystal, while vanadium and molybdenum, among others, can be cited as prime examples of β-stabilizing alloying elements. Zirconium and tin dissolve well in both phases.

The different phases present at room temperature after annealing are subdivided into α-titanium alloys, β-titanium alloys and $(\alpha+\beta)$ -titanium alloys. These alloys are described by, for example, A.D. McQuillan and M.K. McQuillan in "TITANIUM", London, Butterworths Scientific Publications, 1956.

The present invention relates especially to the $(\alpha+\beta)$ titanium alloys. Typical examples of these alloys are the alloys listed in Table I below, for which the strength data at room temperature are also indicated.

Table I

$(\alpha+\beta)$ alloy	Ultimate tensile strength RM [MPa]	0.2%-offset yield strength $R_{P0.2\%}$ [MPa]	Elongation after fracture EL [%]	Reduction of area RA [%]
Ti4Al4Mo2Sn 0.5Si	1115	980	9	20
Ti6Al4V	900	830	10	20
Ti6Al6V2Sn Fe Cu	1035	965	10	15
Ti6Al4Zr2Mo2Sn	900	830	10	20
Ti7Al4Mo	965	900	10	15

In recent years there has been no lack of attempts to improve the static and dynamic mechanical properties of these $(\alpha+\beta)$ titanium alloys by subjecting them to special treatments, i.e., thermomechanical treatments, wherein the materials are first usually hot-worked, since their elongation before reduction of area is small. By means of solution annealing and stabilization, it is then possible to achieve better material properties such as, for example, increased thermal stability and improved creep behavior.

Numerous publications concerning improvements of the mechanical properties of titanium alloys have recently appeared in connection with the International Conference on Titanium of September 10-14, 1984 in Munich in Volume 1 of the Proceedings. By way of example, reference is made here to the papers in that Volume 1 on page 179 ff., page 267 ff., page 327 ff. and page 339 ff. The mechanical properties of highly advanced PM titanium shaped parts are also reported by J.P. Herteman et al. in "Powder Metallurgy International" Vol. 17, No. 3, 1985, pages 116 to 118,wherein the authors have observed that the mechanical properties of a material processed by hot isostatic pressing can be improved by the use of purer oxide-free powder and the adjustment of a suitable structure to such an extent that this so-called HIP material, in its strength values and susceptibility to damage, can be favorably compared with forged materials or is even slightly superior to them. Nonetheless, however, that paper reveals that the values for the ultimate tensile strength (RM) and yield strength (0.2%-offset yield strength $R_{P0.2\%}$) still cannot be raised above 1100 MPa, while the elongation (breaking elongation EL) does not rise above 17% and the reduction of area (RA) reaches hardly more than 40%.

Since, besides the chemical industry as the largest consumer, it is still the aerospace industry that is and must be especially interested in titanium alloys having improved mechanical properties, the problem addressed by the present invention was to make available a process for improving the static and dynamic mechanical properties of $(\alpha+\beta)$-titanium alloys by thermomechanical treatment and thus $(\alpha+\beta)$-titanium alloys that exhibit ultimate which, in addition, are also able to withstand a number of load cycles to fracture which is greater than those of $(\alpha+\beta)$ titanium alloys of comparable composition obtained by processes in common use heretofore.

The working by more than 60% required initially according to the invention for the $(\alpha+\beta)$ titanium alloys produced by melting and forging and/or hot isostatic pressing, some examples of which were indicated above, can be suitably accomplished by means of forging, pressing, swaging, rolling or drawing. Of the cited alloys, the alloy Ti6Al4V has proved especially suitable for the process according to the invention, but the alloys Ti6Al6V2Sn, Ti7Al4Mo and Ti6Al2Sn4Zr2Mo can also be successfully thermomechanically treated.

According to the invention, the structure of the alloys should be stress-relieved by heating between the individual deformation steps, making certain that this microstructure is not completely recrys tallized. For this reason, lenghty intermediate annealings are to be avoided in any case. Illustrated by way of example in Figure 5a is the structure of the high-strength alloy Ti6Al4V after swaging at 850 °C at 1000-times magnification.

The shaped part with the desired final dimensions is then tempered, i.e., annealed for 2 to 4 min at the transus. It is known that the transus, i.e., the temperature of allotropic transformation of, for example, pure titanium, lies at 885 °C. This means that the hexagonal crystal lattice of α-titanium that exists at temperatures below 885 °C goes over at higher temperature into the cubic body-centered lattice of β-titanium.

darauf

For the alloy Ti6Al4V the transus lies at 975 °C, but also depending on oxygen content. The alloys are quenched after the annealing, suitable means for the quenching being familiar to a person skilled in the art. Preferably, however, the quenching is done with water, with oil or with both means. The structure of the alloy already mentioned in connection with Figure 5a is illustrated in Figure 5b, again at 1000-times magnification. This figure shows the interstitial insertion of globular, relatively large α particles (μm range) in the $(\alpha+\beta)$ structure, while in the $(\alpha+\beta)$ region one can observe extremely small precipitates of α lamellae which are interstitially inserted in the β structure.

To achieve stabilization of this structure, the quenched shaped parts are then aged at temperatures in the range of from 400 °C to 600 °C, preferably for 2 h at 400 °C to 500 °C. This coarsens the $(\alpha+\beta)$ precipitates without changing the large α grains. This is shown by the structure reproduced in Fig. 6a for the alloy Ti6Al4V chosen as an example. As can be seen in the TEM picture (Fig. 6b), the α particles exhibit dislocations and low-angle grain boundaries, i.e., these α particles are polygonized and not recrystallized. As is known to a person skilled in the art, alloying elements in titanium alloys can influence the transus. Al und O extend the α region of the alloys to higher temperatures. The elements V, Mo, Mn and Cr extend the β region of the alloys, i.e., the temperature of the transus falls. For the alloy Ti6Al4V, the transus of pure titanium is shifted to a higher temperature. Zn and Sn are neutral elements in this respect.

wir ± 600-700

For the $(\alpha+\beta)$ titanium alloys used in practice, i.e., especially Ti6Al4V, but also the alloys Ti6Al6V2Sn, Ti7Al4Mo and Ti6Al2Sn4Zr2Mo, an $(\alpha+\beta)$ structure is present at room temperature. The structure can be changed by working and annealing, and various mechanical properties can be adjusted in this manner. The material is first to be greatly deformed, i.e., by > 60 %, at about 50 °C above the recrystallization temperature of ca. 800 °C, i.e., at 850 °C, so that it is intensively plastically worked and thereby strainhardened. By solution annealing below 950 °C and tempering for 2 h at 500 °C, a globular $(\alpha+\beta)$ structure is adjusted. Upon annealing at between 950 °C and 975 °C and tempering at 500 °C, a fine $(\alpha+\beta)$ structure is adjusted, namely, very fine equiaxed primary α embedded in lamellar $(\alpha+\beta)$ matrix structure, with outstanding mechanical properties. In contrast, upon annealing above 975 °C and tempering, a lamellar structure is formed whose ductility is sharply decreased. The fine $(\alpha+\beta)$ structure is a prerequisite for an increase of the ultimate tensile strength and 0.2 %-offset yield strength with a simultaneous increase of the elongation and of the reduction of area. In addition, the fatigue strength for a large number of load cycles is doubled in comparison to conventional materials.

wir 975 °C ± 15 K

? aber kein uniform

The outstanding mechanical properties of the $(\alpha+\beta)$ titanium alloys produced according to the invention, clearly improved over the comparison alloys known heretofore, are illustrated in the following Table II and in the appended diagram (Fig. 3). The values of ultimate tensile strength, 0.2 %-offset yield strength, elongation and reduction of area are far above the minimum values specified in DIN Standard No.

allotropic transformation (transus α-β) ≠ recrystallization temp.

17 851. Table II also indicates the values determined for the modulus of elasticity. Although it is true that the alloy Ti6Al4V that is only HIP-deformed also meets the DIN Standard, the material produced according to the invention far surpasses it in all values, it being especially surprising that along with the increased strength the ductility of the material is also considerably increased, namely, by about 30 %.

The fatigue strength of the alloy was measured in the Amsler-Pulser under the conditions R = 0.1, k_t = I and the frequency 130 ± 19 Hz. The upper Woehler curve shown in the diagram (Fig. 4) for the material produced according to the invention exhibits, throughout the entire frequency range and for a number of load cycles up to 10^7, sharply improved cyclic fatigue strengths in comparison to the materials produced according to the processes commonly used heretofore (lower Woehler curve). The properties were improved by 40 % in the ultimate tensile strength and by 100 % in the fatigue strength.

In one example of application, screws 8 mm in diameter were produced and tested for their cyclic fatigue strength. Whereas conventional material was able to endure a maximum of 30,000 periodic stress changes until fracture, after application of the thermomechanical treatment according to the invention the number of periodic stress changes until fracture was 360,000, i.e., greater by a factor of 12, with the same load.

The transus increases with higher oxygen content. If the oxygen content is higher, the annealing at 975 °C is below the transus. But if the oxygen content is lower, the annealing at 975 °C is above the transus.

On the basis of the described improvement of the static and dynamic mechanical properties of the materials produced according to the invention, it is obvious that by its use the range of application of high-strength ($\alpha + \beta$) alloys can be considerably extended, both for static and dynamic loads, which is of great significance especially for the aerospace industry.

The mechanical properties of the alloy Ti6Al4V after the annealing treatment are illustrated by curves in Figures 1 and 2, in one as a function of the degree of deformation (Fig. 1) and in the other as a function of the solution temperature (Fig. 2).

Table II

Static mechanical properties

	Ultimate tensile strength RM [MPa]	0.2%-offset yield strength $R_{P0.2\%}$ [MPa]	Elongation after fracture EL [%]	Reduction of area RA [%]	Modulus of elasticity E [GPa]
DIN Standard 17 851	910	840	10	25	110
HIP densification 930°C 2.5 h 1.94 kbar	967.3	900.0	14.5	41.4	128
HIP densification, extruded 900°C, swaged 63.5% at 850°C, heat-treated at 975°C/3 min /water quenching; 500°C 2 h air cooling	1298.0	1203.4	15.1	54.3	116.1

Claims

1. Process for improving the static and dynamic mechanical properties of $(\alpha+\beta)$-titanium alloys by thermomechanical treatment, wherein the alloys,produced by melting and forging, hot isostatic pressing, extrusion and/or other per se known processes for compacting and processing of pure or contaminated powders, are deformed by more than 60 % with simultaneous strain-hardening at a temperature just above the recrystallization temperature of the relevant alloys in one or more steps, with structure stress-relief heatings being performed without complete recrystallization between these individual steps, the shaped part is then tempered for about 2 to 4 minutes near the transus of the alloy, quenched and then aged at temperatures of about 400° - 600°C.

2. Process in accordance with Claim 1, characterized in that the alloys are deformed by forging, pressing, swaging, rolling or drawing.

3. Process in accordance with Claim 1, characterized in that the quenching of the shaped part is performed with water and/or oil.

4. Process in accordance with Claim 1, characterized in that the shaped part is first tempered for 3 minutes at temperatures between about 950°C and 980°C and quenched, and is then aged for 2 hours at 450°-550°C.

5. Process in accordance with Claim 2, characterized in that the shaped part is first tempered for 3 minutes at temperatures between about 950°C and 980°C and quenched, and is then aged for 2 hours at 450°C-550°C

6. Process in accordance with Claim 1, characterized in that $(\alpha+\beta)$-titanium multicomponent alloys based on Ti4AlX or Ti6AlX are used, where X signifies one or more alloying elements from the group consisting of vanadium, molybdenum, zirconium, tin, iron, copper and silicon, are used.

7. Process in accordance with Claim 1, characterized in that the alloy Ti6Al4V is deformed by 90% by hammering at 850°C, the shaped part is then tempered for 3 minutes at 975°C, quenched with water and then aged for 2 hours at 500°C in air.

8. Process in accordance with Claim 4, characterized in that $(\alpha+\beta)$-titanium multicomponent alloys based on Ti4AlX or Ti6AlX are used, where X signifies one or more alloying elements from the group consisting of vanadium, molybdenum, zirconium, tin, iron, copper and silicon, are used.

9. Process in accordance with Claim 4, characterized in that the alloy Ti6Al4V is deformed by 90% by hammering at 850°C, the shaped part is then tempered for 3 minutes at 975°C, quenched with water and then aged for 2 hours at 500°C in air.

10. Process in accordance with Claim 6, characterized in that $(\alpha+\beta)$-titanium multicomponent alloys based on Ti4AlX or Ti6AlX are used, where X signifies one or more alloying elements from the group consisting of vanadium, molybdenum, zirconium, tin, iron, copper and silicon, are used.

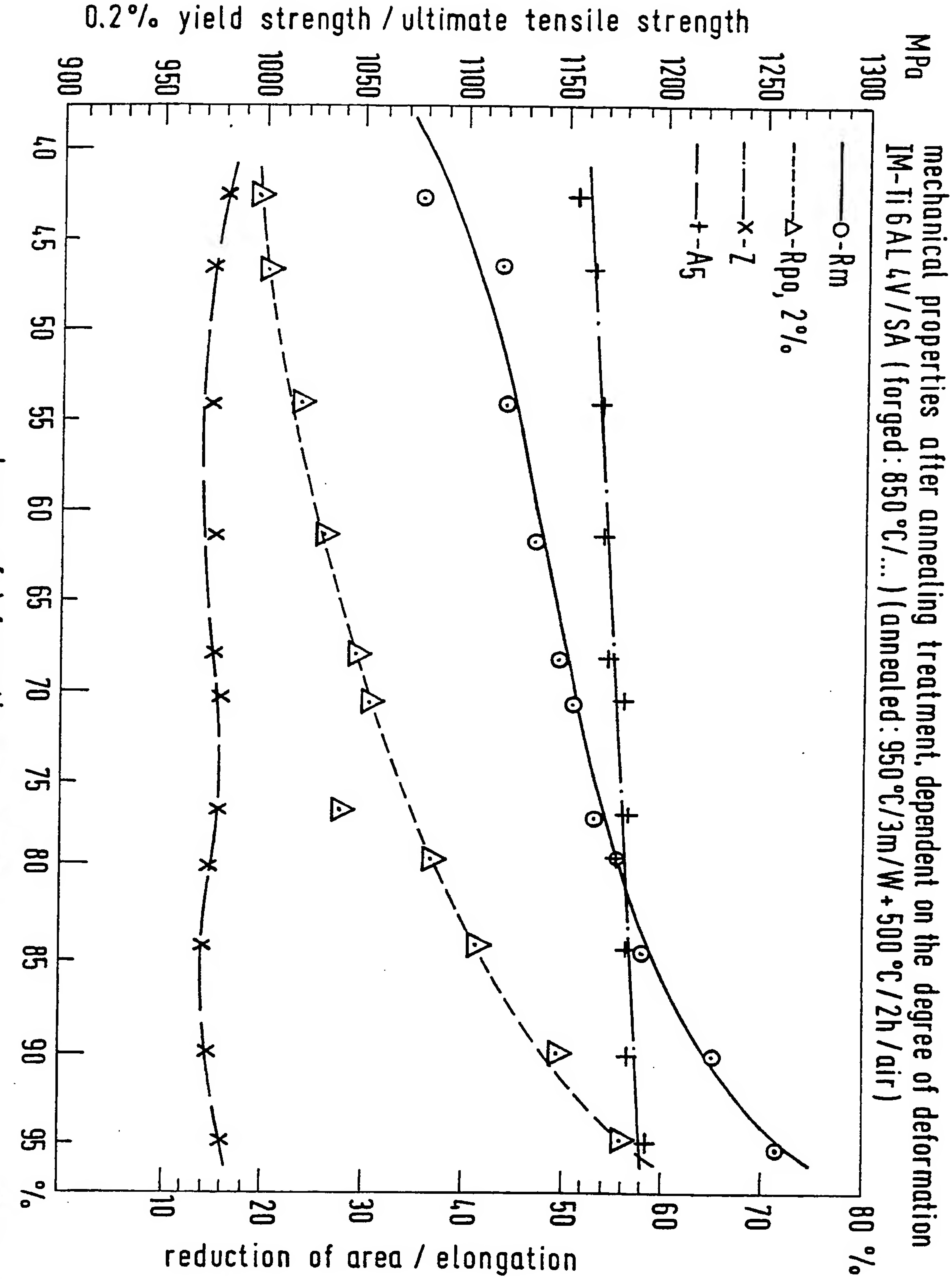

mechanical properties after annealing treatment, dependent on the degree of deformation
IM-Ti 6AL 4V / SA (forged: 850°C/...) (annealed: 950°C/3m/W + 500°C / 2h / air)
—o— Rm
---Δ--- Rpo, 2%
-·-x-·- Z
—+— A5
MPa
1300
1250
1200
1150
1100
1050
1000
950
900
0.2% yield strength / ultimate tensile strength
40
45
50
55
60
65
70
75
80
85
90
95
%
degree of deformation
80 %
70
60
50
40
30
20
10
reduction of area / elongation

FIG. 1

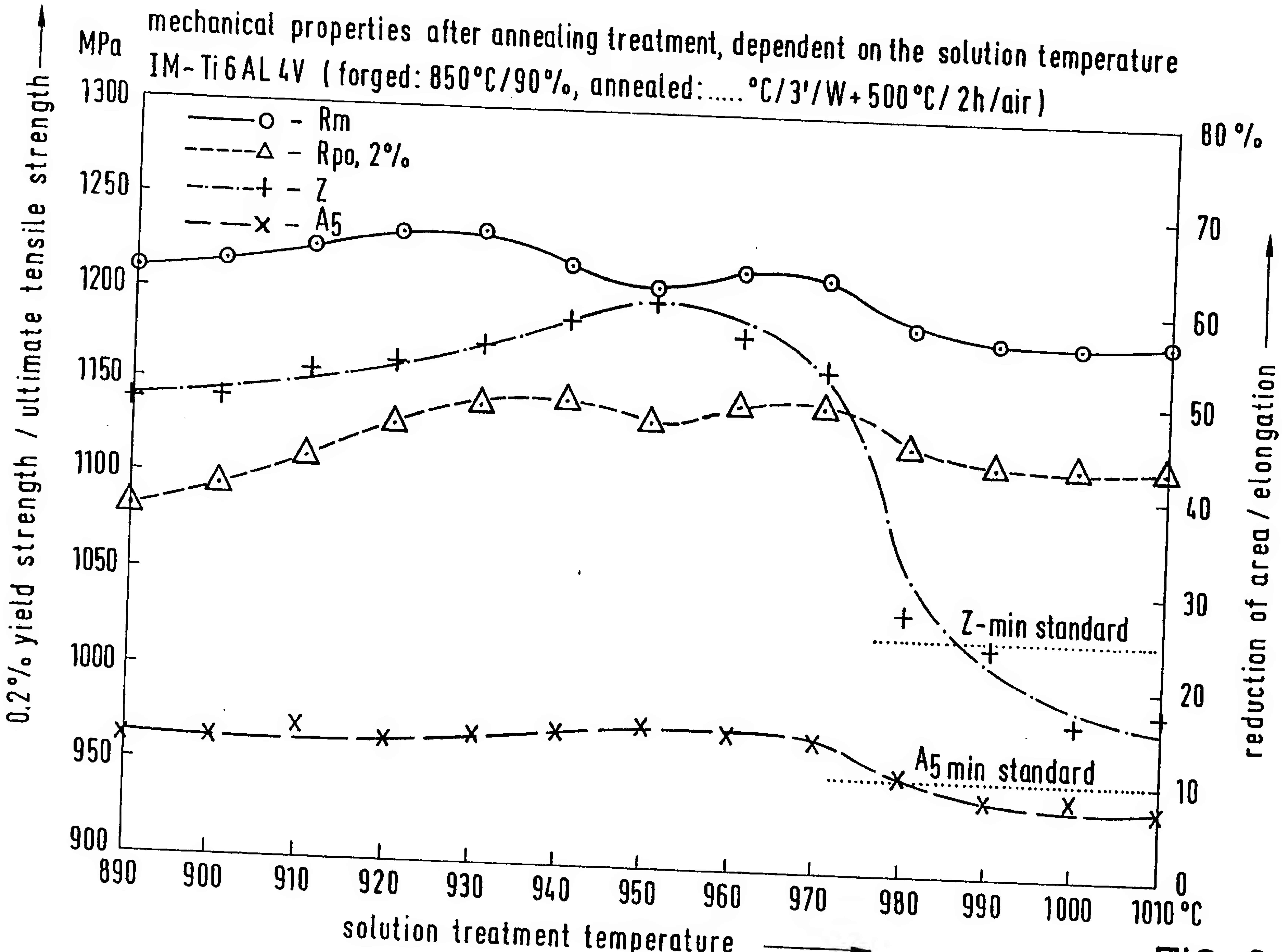

mechanical properties after annealing treatment, dependent on the solution temperature
IM-Ti6AL4V (forged: 850°C/90%, annealed:.....°C/3'/W+500°C/2h/air)
MPa
1300
1250
1200
1150
1100
1050
1000
950
900
0.2% yield strength / ultimate tensile strength
—o— Rm
---Δ--- Rpo, 2%
-·-·+ Z
— —x— A5
80 %
70
60
50
40
30
20
10
0
reduction of area / elongation
Z-min standard
A5 min standard
890
900
910
920
930
940
950
960
970
980
990
1000
1010 °C
solution treatment temperature

FIG. 2

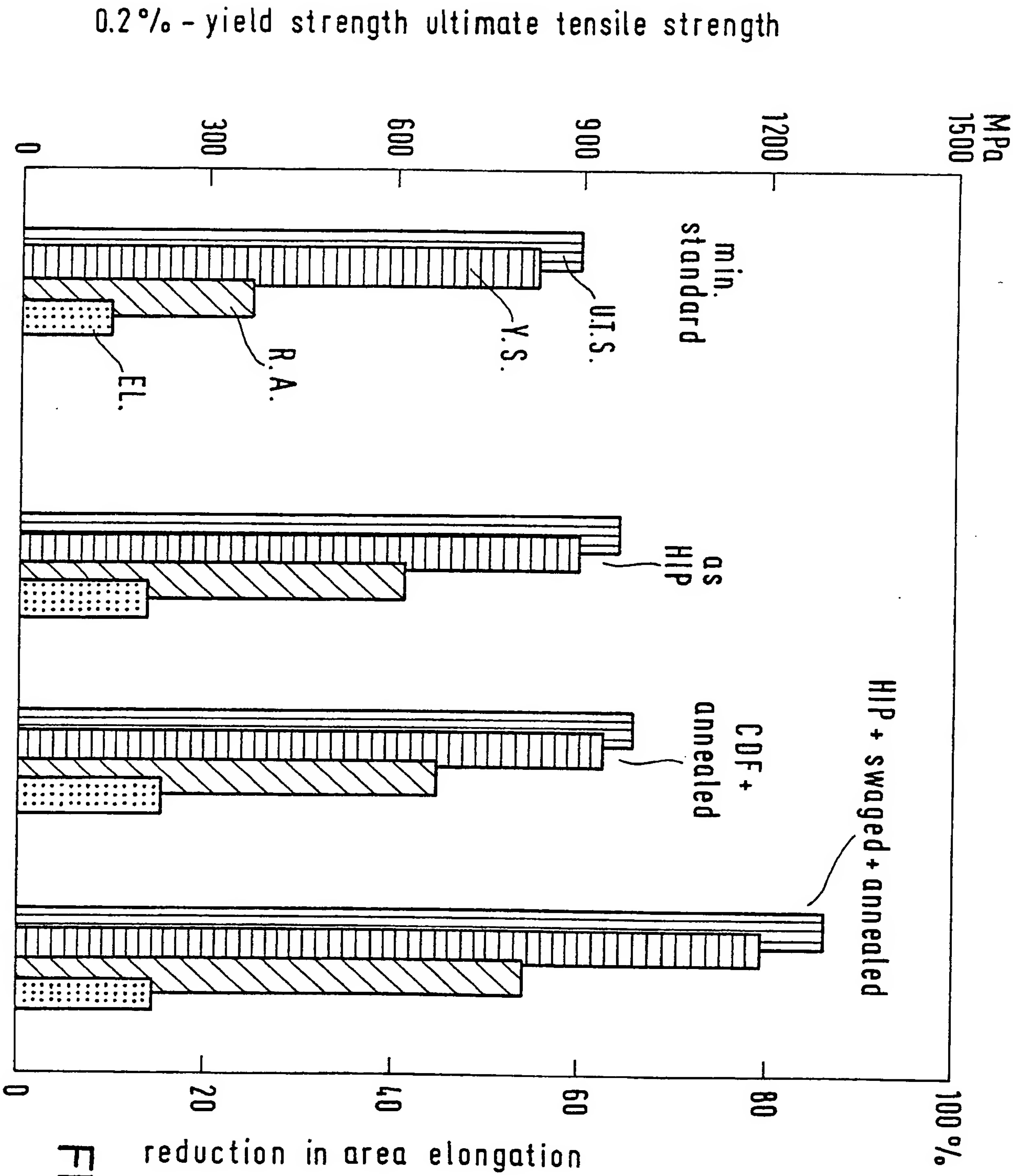

0.2 % - yield strength ultimate tensile strength
MPa
0
300
600
900
1200
1500
min. standard
U.T.S.
Y.S.
R.A.
EL.
as HIP
CDF + annealed
HIP + swaged + annealed
0
20
40
60
80
100 %
reduction in area elongation

FIG. 3

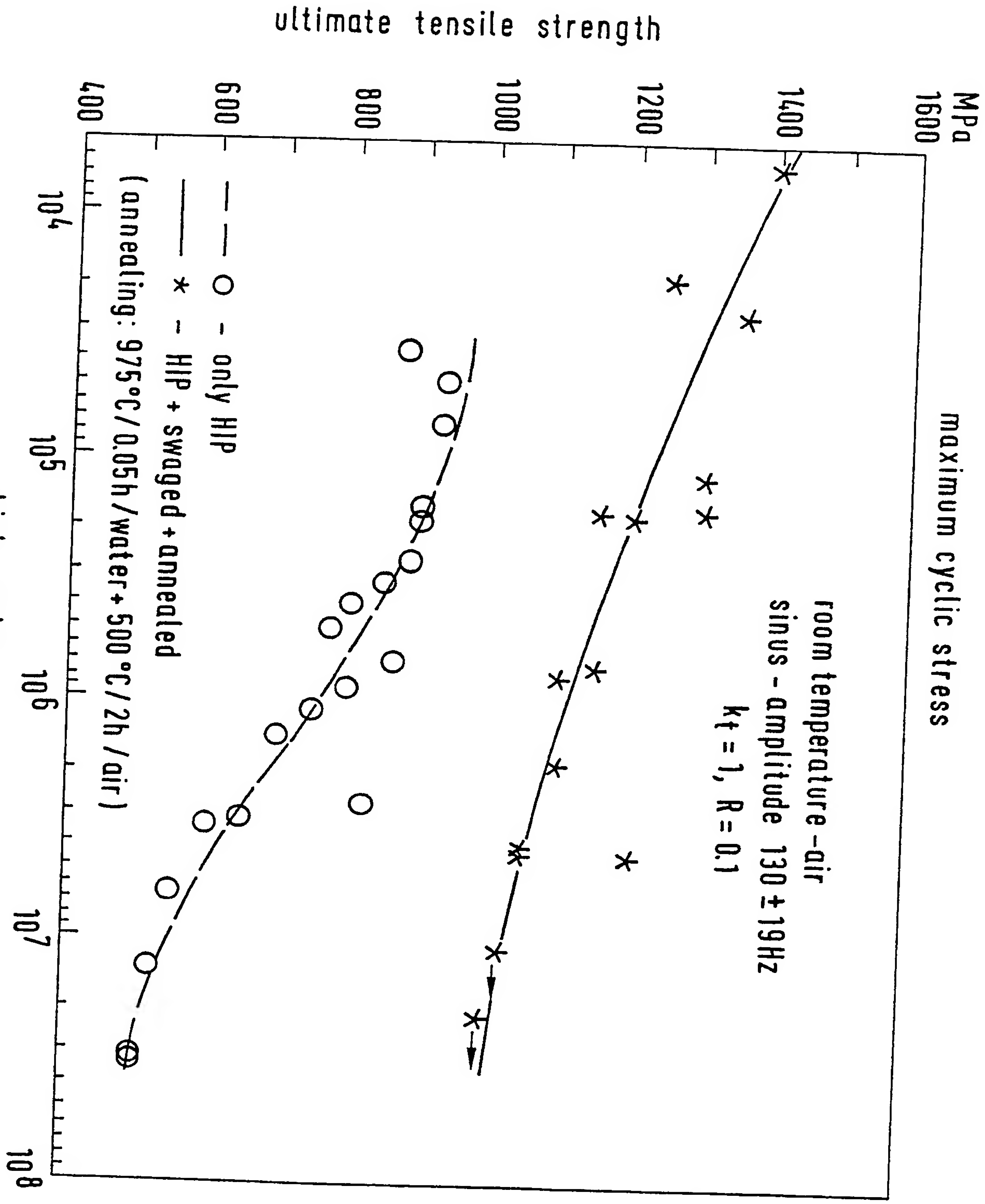
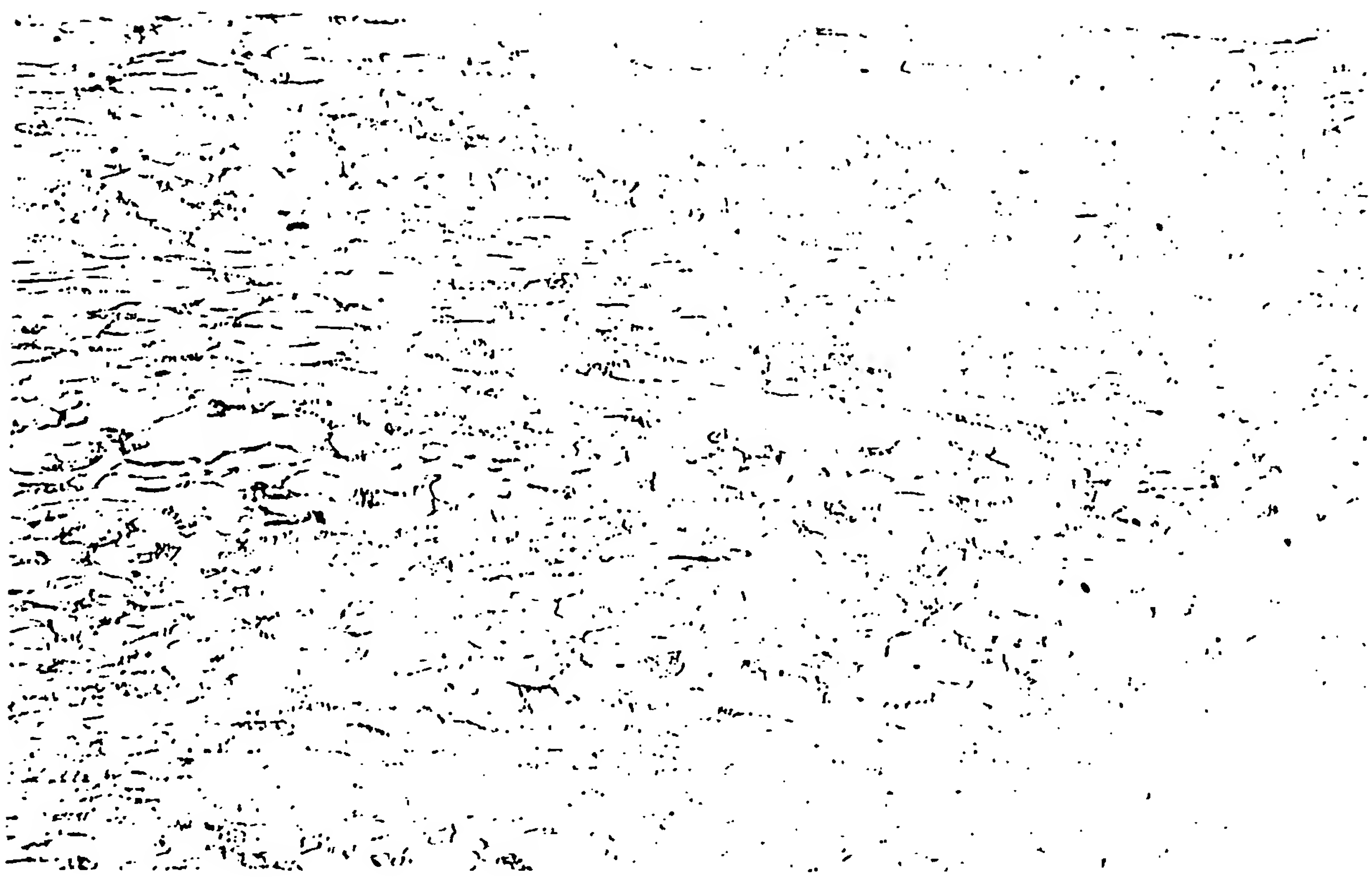

ultimate tensile strength
MPa
1600
1400
1200
1000
800
600
400
maximum cyclic stress
room temperature-air
sinus-amplitude 130 ± 19Hz
k_t = 1, R = 0.1
O - only HIP
* - HIP + swaged + annealed
(annealing: 975°C/0.05h/water + 500°C/2h/air)
10^4
10^5
10^6
10^7
10^8
high cycles

FIG. 4



1000 x

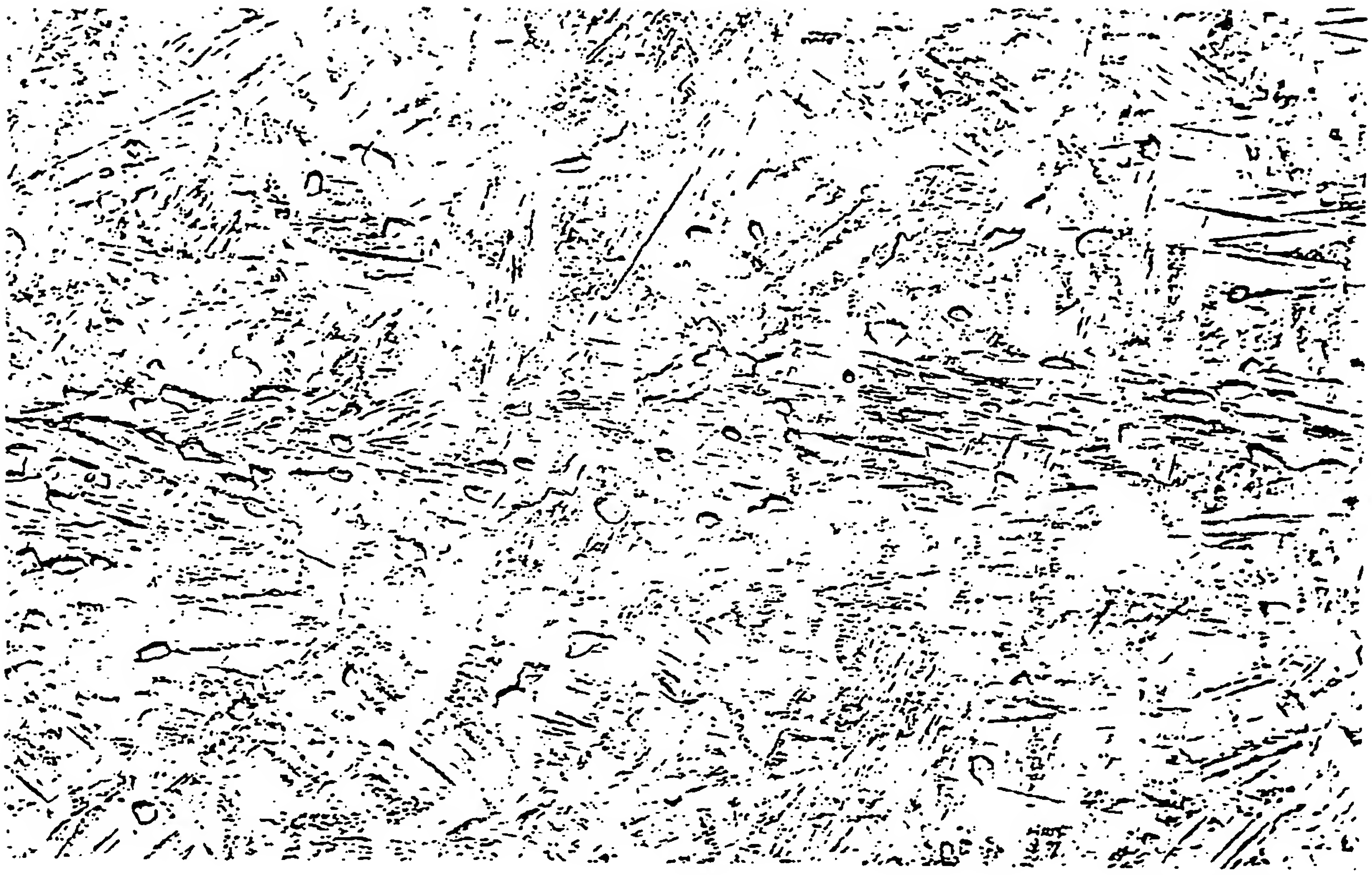
Fig. 5a Ti6Al4V
64 % deformed at 850 °C

+

viel
zu niedrige Temperatur

1000 x

Fig. 5b Ti6Al4V
fine (α + β) structure
975 °C/3 min/water
64 % deformed at 850 °C



1000 x

Fig. 6a Ti6Al4V
fine (α + β) structure
975 °C/3 min/water + 500 °C/2 h
64 % deformed at 850 °C

Fig. 6b TEM picture
fine (α + β) structure
975 °C/3 min/water + 500 °C/2 h
64 % deformed at 850 °C

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EP 0 254 891 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 87 10 9433

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	METAL PROGRESS, vol. 129, no. 7, June 1986, pages 41,42,47-51; E.J. KUBEL, Jr.: "Titanium alloy technology update" * Page 42, centre column, line 20 - right-hand column, line 33 *	1	C 22 F 1/18
A	GB-A-1 160 829 (CONTIMET GmbH) * Claim 1 *	1	
A	FR-A-2 116 260 (N.A. GREKOV et al.) * Claims 1,4 *	1	
A	FR-A-2 162 856 (UNITED AIRCRAFT CORP.) * Claims 1,9 *	1,4	
A	ZEITSCHRIFT FÜR METALLKUNDE, vol. 67, no. 3, March 1976, pages 148-151; K.E. MANN et al.: "Festigkeitseigenschaften eines aus dem Beta-Gebiet isotherm umgewandelten Gesenkpressteiles der Titanlegierung Ti7Al4Mo"		TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 22 F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	08-12-1988	GREGG N.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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